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HIGH-TEMPERATURE STRUCTURAL COMPONENTS

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COATED REFRACTORY METALS FOR  
HIGH-TEMPERATURE STRUCTURAL COMPONENTS

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SUMMARY

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The significant results of several studies at the Langley Research Center of the NASA to investigate the utilization of refractory metals as structural materials in high-temperature oxidizing environments are presented. These results include the elevated-temperature tensile strengths of several advanced columbium alloys.

The effect of coating application and subsequent high-temperature exposure on the tensile properties of one columbium alloy for 11 silicide-based coatings under investigation is presented. In general, the tensile strength of the substrate is not severely affected from room temperature to 3,000° F by the application of a protective coating. Elongation, while not severely affected at elevated temperature, is reduced at room temperature. Room-temperature elongation of the coated columbium is further reduced after high-temperature exposure in air. As a result of oxidation tests on a coated molybdenum alloy, a failure mechanism is proposed for silicide-based coatings. This mechanism is based on the transformation of the protective amorphous silica outer layer of the coating at high temperatures to a crystalline form of silica which is less protective. This crystalline form of silica, cristobalite, undergoes a large volume change when heated or cooled. This volume change is responsible for the reduced tolerance of silicide-based coatings to thermal cycling.

The results of an experimental study to determine the performance of thin-gage refractory metals in heat-shield panels indicated that lightweight (1.1 lb/ft<sup>2</sup>) panels utilizing thin-gage sheet and flexible supports are capable of withstanding dynamic pressures to 1,500 psf, and the oxidation resistance of coated molybdenum sheet material in a representative structure is inferior to that of small coated coupons.

AUTHOR

INTRODUCTION

This talk will present the highlights of several investigations concerned with the use of refractory metals in high-temperature oxidizing environments. These programs are concerned primarily with the application of coated, thin-gage refractory metals to the thermal protection systems of lifting reentry vehicles.

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These studies include the high-temperature mechanical properties of some advanced columbium alloys and the effect of coating application on the tensile properties of a typical columbium alloy. A failure mechanism which is useful in explaining the reduced tolerance of silicide-based coatings on molybdenum alloys to thermal cycling is presented. The results of a program which involved the design, fabrication, and testing of two representative refractory-metal heat-shield panels will also be presented.

## RESULTS OF INVESTIGATIONS

Tensile properties of columbium alloys.- Although the columbium alloys have less desirable high-temperature mechanical properties (such as tensile strength, modulus of elasticity, and creep resistance) than molybdenum alloys, they have been selected for a variety of high-temperature applications because of their ductility and ease of fabrication (ref. 1). The development of columbium alloys which have improved high-temperature tensile properties with little or no sacrifice in fabricability has resulted in a second generation of columbium alloys. The results of tensile tests on thin-gage sheet material of three of these advanced alloys (B-66, D-43, and Cb-752) are compared with two typical first-generation alloys (D-36 and FS-82)<sup>1</sup> in figure 1.

As can be seen, the tensile strengths of the advanced alloys show a general improvement over the older alloys in the temperature range of most interest for columbium alloys (2,000° to 2,600° F). These three advanced alloys are commercially available and have been selected for advanced fabrication studies by other investigators (ref. 2).

Evaluation of coatings for columbium.- The utilization of columbium alloys in high-temperature oxidizing environments is contingent on the development of a coating which will protect the columbium substrate from oxidation. In addition, the coating should not seriously alter the mechanical properties of the substrate during application of the coating or in subsequent service. The Langley Research Center is currently investigating 11 commercially available silicide-based coatings for columbium alloys. The substrate chosen for this investigation was 20 mil D-36 sheet in the recrystallized condition.

The effect of the application of these silicide-based coatings on the tensile strength of the D-36 sheet is shown in figure 2. The smooth curves represent the average tensile strength and elongation of the uncoated D-36 sheet. Tensile tests were performed to study a number of coatings at room temperature, 2,000° F, and 2,400° F. The average values and the scatter of these data are indicated by circles and tick marks, respectively. The number above the scatter band is the number of coatings included in the average. It can be seen that

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<sup>1</sup>Alloy compositions are as follows:

B-66 (Cb-5Mo-5V-1Zr)  
D-43 (Cb-10W-1Zr-.1C)  
Cb-752 (Cb-10W-2.5Zr)  
D-36 (Cb-10Ti-5Zr)  
FS-82 (Cb-34Ta-.75Zr)

there was little or no change observed in the room-temperature tensile strength between the "average" coated specimen and the base material. A single coating was tested from 1,600° F to 3,000° F. These data are shown as squares and can be seen to follow the uncoated material curves rather closely which indicates that this particular coating did not significantly affect the high-temperature strength and elongation of the base material. The average room-temperature elongation, however, was reduced approximately 50 percent. It has not yet been determined whether this reduction in elongation was caused by coating constituents or an increased interstitial content, either or both of which may have an embrittling effect on the base metal. At 2,000° F and 2,400° F there was little or no change observed in either the strength or elongation between the coated specimens and the base material. In all cases the tensile strength was based on the cross-sectional area before coating. All of the elevated-temperature tests were performed by resistance heating the specimens. This procedure may account for the low elongation values of the uncoated material and some of the scatter in the coated specimens.

The effect of high-temperature exposure on the room-temperature tensile strength and elongation of coated D-36 sheet material is shown in figure 3. The average tensile strength and elongation of the coatings under study in the as-coated condition and after 1 and 8 hours exposure to 2,400° F in air is presented. This figure indicates that there is no appreciable change in the average tensile strength of the coated D-36 up to 8 hours exposure at 2,400° F. The average elongation, however, continued to decrease as exposure increased indicating that either the components of the coatings or penetrating atmospheric gases were embrittling the substrate. The scatter in elongation data after exposure shows a large variation between coatings and indicates that if reduced elongation at room temperature is undesirable after high-temperature exposure, some of the coatings under investigation would not be suitable. The heavy horizontal lines in figure 3 are for the uncoated D-36 substrate after comparable exposures to 2,400° F in a vacuum of  $10^{-5}$  torr and show no significant change in either elongation or strength.

A failure mechanism associated with silicide-based coatings on Mo-0.5 Ti.-  
The applications which are most often considered for coated refractory metals involve thermal cycling in addition to steady-state exposure at high temperatures. A previous investigation (ref. 3) was concerned with the protection of molybdenum alloy sheet by silicide-based coatings.

This study performed at 2,500° F in static, ambient-pressure air, indicated that thermal cycling resulted in a severe reduction in coating life. Five of the six coatings which were investigated were either pure or slightly modified silicide-based coatings. One of the coatings was highly modified and included boron as a coating modifier. These two classes of coatings will hereinafter be referred to as silicide and boron-modified silicide coatings, respectively. Typical specimen weight change curves as a function of exposure time for both cyclic and continuous exposure are presented in figure 4 for both the silicide and the boron-modified silicide-based coatings. A specimen weight loss of 10 percent is defined as failure. The following observations can be made from this figure:

1. The life of both coating types is reduced when the coated specimens are thermally cycled.

2. The boron-modified coating was superior to the silicide coatings in both the continuous and cyclic exposures.

3. When continuously exposed, silicide-coated specimens typically exhibited a slight increase in weight preceding a rapid weight loss. The boron-modified coated specimens, on the other hand, exhibited little or no weight change preceding failure and failed in a gradual manner.

4. The continuously exposed silicide-coated specimens initially lost weight, while the cyclically exposed specimen exhibited a net weight gain which reached a maximum preceding a rapid weight loss to failure.

In addition to the noted weight changes, X-ray examination of the failed specimens, after both continuous and cyclic exposure of the silicide coatings, revealed significant amounts of a crystalline form of  $\text{SiO}_2$  on the exposed surfaces. Little or no evidence of this crystalline form of  $\text{SiO}_2$  was noted on the surface of the boron-modified coated specimens after either cyclic or continuous exposure. As a result of this program, a failure mechanism is proposed which attempts to explain at least one phenomenon which is operative in coating failure. The failure mechanism to be discussed is associated with the formation of amorphous silica on the surface of the coating and its transformation to a crystalline form and will be described with the aid of the next two figures. The first, figure 5, shows a schematic representation of the various phases which are present in the coating-substrate system from coating application to failure for a typical silicide-based coating on a molybdenum substrate.

Silicide-based coatings for molybdenum alloys are composed primarily of  $\text{MoSi}_2$ . The oxidation resistance of  $\text{MoSi}_2$  is attributed to the formation of an impervious layer of  $\text{SiO}_2$  on the surface of the coating when the  $\text{MoSi}_2$  oxidizes. Formation of the  $\text{SiO}_2$  can be the result of two different oxidation reactions. One of these reactions results in the formation of volatile  $\text{MoO}_3$  and  $\text{SiO}_2$  and the other results in the formation of  $\text{Mo}_5\text{Si}_3$  and  $\text{SiO}_2$ . Although both reactions are probably taking place simultaneously during the initial stages of the silica formation, the reaction to form  $\text{MoO}_3$  is favored and the coated specimen would lose weight. As the  $\text{SiO}_2$  layer grows and the activity of oxygen at the oxidizing interface is reduced, the reaction to form  $\text{Mo}_5\text{Si}_3$  and  $\text{SiO}_2$  is favored (ref. 4).

The  $\text{SiO}_2$  is amorphous as formed, but after a period of incubation, cristobalite is nucleated and forms. This silica phase change results in a sharp increase in the rate of oxygen diffusion (ref. 5). The diffusing oxygen then reacts with the remaining coating and/or the substrate. Any  $\text{MoO}_3$  formed as result of coating and/or substrate oxidation would be highly volatile at the test temperature. If the oxidation products could not escape as fast as formed, the specimen would gain weight. As the pressure of the  $\text{MoO}_3$  increased, the

coating would rupture and a rapid weight loss would occur. The weight gain preceding a rapid failure and the observation of  $\alpha$  cristobalite on the failed surface, previously noted for the silicide coating, supports this mechanism of failure. The boron-modified silicide coating had the best oxidation resistance of those tested, did not have large amounts of the  $\alpha$  cristobalite on the failed surfaces, did not show a weight gain prior to failure (fig. 4), and usually failed in a gradual manner. Although this mechanism, the formation of cristobalite on the coating surface, appears to satisfactorily describe at least one phenomenon associated with failure in the continuous exposure oxidation tests, it does not explain the sharp reduction in coating life for both coating types and the net weight gain observed on the silicide-coated specimens when the specimens were cyclically exposed. The only way that  $\text{MoSi}_2$  can gain weight during oxidation is by the formation of  $\text{Mo}_5\text{Si}_3$  and  $\text{SiO}_2$ . This reaction is favored when the activity of the oxygen at the oxidizing interface is low (fig. 5) which would not be the case if the oxidizing surface was on the surface of the coated specimen. Since the surface of the failed cyclically exposed silicide-coated specimens also revealed large amounts of  $\alpha$  cristobalite, it was concluded that the  $\alpha$  to  $\beta$  cristobalite phase transformation which occurred during each thermal cycle was responsible for the net weight gain which occurred prior to rapid weight loss and failure. The change in expansion which is associated with this transformation is shown in figure 6. This figure also includes the thermal expansion characteristics of  $\text{MoSi}_2$ , Mo, and amorphous silica. The shrinkage associated with the  $\beta$  to  $\alpha$  transformation may be sufficient to crack the  $\text{SiO}_2$  on the outside of the coating. When the specimen was reheated, any cracks in the oxide layer would seal after the cristobalite transformation. Because the  $\text{MoSi}_2$  phase of the coating would still be in tension at this temperature, any gases remaining in the cracked coating or at the  $\text{MoSi}_2$  -  $\text{SiO}_2$  interface would be trapped. The reduced activity of the trapped oxygen would cause the reaction to form  $\text{Mo}_5\text{Si}_3$  and  $\text{SiO}_2$  to be favored and the specimens would gain weight. The specimen would continue to gain weight until complete coating breakdown occurred. This continued reexposure of virgin coating would result in a more rapid deterioration of the coating and reduce coating life.

As noted, the specimens with the boron-modified coating did not gain weight (fig. 4) during the cyclic tests. The boron-modified silica would not be expected to experience the large shrinkage associated with the cristobalite transformation and as a result no oxygen would be trapped. As in the continuous exposure tests, this boron modification would also increase the lifetime of the coating by retarding the nucleation and growth of the cristobalite phase.

Although this hypothesis is useful in explaining the reduced coating life as a result of thermal cycling, it is recognized that the proposed mechanism is not applicable for all environmental effects and that a variety of mechanisms, such as the formation of a low-temperature "pest" and coating instability caused by high-temperature—low-pressure effects have been associated with the failure of silicide-based coatings (refs. 6 and 7).

Columbium and molybdenum heat-shield panels.- All of the investigations previously described are in support of the same objective - the effective application of coated refractory metals, particularly in thin gages, as structural components in aerospace vehicles. One of the most important of these applications is the heat shields of a radiatively cooled thermal protection system. In order to determine the capabilities and limitations of a thermal protection system utilizing thin-gage refractory-metal heat shields, a program was undertaken to design, fabricate, and test representative heat-shield panels. This program would integrate the results of previous investigations and provide the design, fabrication, and performance experience which is necessary for the development of a reliable thermal protection system.

Three panels were fabricated for this program. One was fabricated from a nickel-base superalloy to substantiate the feasibility and performance of the chosen design and will not be discussed. The other two panels utilized refractory metals in their construction. One was fabricated with a columbium alloy (FS-82), and the other from silicide-coated Mo-0.5Ti. The pertinent design details are shown in figure 7. The panels are approximately 20 inches long and 20 inches wide. They consist of a 10-mil corrugated refractory-metal outer skin, a layer of insulation, a corrugated superalloy substructure panel, and weighed approximately 1.1 lb/ft<sup>2</sup>. The outer skin consisted of three subpanels which were attached to the substructure with refractory-metal clips. These clips extended into slots machined into channels and holes in the clips to secure the skin panels. The clips were spot welded to the columbium skin and riveted to the molybdenum skin. The rivets were designed to provide separation between clip and skin for more complete coating of the sheet material in the rivet area. After forming the molybdenum heat-shield components, the skin, clips, and rivets were coated. The clips were riveted to the three subassemblies. These subassemblies were then recoated. The assembly of the columbium skin to its substructure presented no difficulties other than the proper alignment of the clips in the channel slots. The molybdenum heat shields were distorted during coating application. This distortion required widening of the slots in the channels. Several clips were broken before assembly could be accomplished.

The columbium panel has been subjected to Mach 3 airflow and dynamic pressures of 1,500 pounds per square foot with the corrugations oriented both perpendicular and parallel to the airflow to substantiate the lightweight flexible skin and clip design. Although the heat shield exhibited some motion for both orientations of airflow, it did not flutter, and examination after testing revealed no damage to any of the panel components.

In order to evaluate the performance of this design under realistic thermal loads, the coated molybdenum alloy panel was subjected to five simulated reentry heating cycles in still air with a quartz tube heater. The thermal cycle was programed to subject the panel skin to 2,400° F for 5 minutes and to temperatures above 1,500° F for 45 minutes during each 1-hour cycle. During these tests the maximum temperature of the superalloy panel substructure and clip channels was 1,510° F and 1,730° F, respectively. Both of these temperatures are well within the capability of superalloys. The temperature response and distribution through the panel were in close agreement with calculations.

Coating performance was difficult to ascertain both because of the complexity of the structure and because of the insidious nature of coating failures which may not reveal the full extent of the substrate damage. Radiographic examination of the panel between cycles was found to be useful for determining the extent of substrate damage. Figure 8 shows a portion of coated molybdenum shield after 5 cycles. The radiograph (fig. 8(b)) indicates damage which was not visually evident. Figure 8(c) shows the surface after removal of unsupported coating and confirms the usefulness of the radiographic technique.

Although oxidation damage was evident in the clip and support areas (about 92 percent of the clips were damaged) and on the edges of the shield, the panel was still self-supporting and capable of functioning as a heat shield after five heating cycles. Whether or not it was capable of withstanding aerodynamic loads was not determined.

The results of this program suggest the following:

1. Shield subassemblies should be small to minimize the effects of coating distortions.
2. Areas of discontinuities such as edges, rivets, and attachment clips should be minimized and extreme care in the design and fabrication of these areas should be exercised to avoid premature coating failure.
3. The oxidation resistance of coated molybdenum sheet material in a representative structure is inferior to that of small coated coupons.

Temperature measurement on coated refractory metals is difficult because of thermocouple reactions with the coating. This problem was satisfactorily solved in this investigation with spring-loaded thermocouple assemblies. The construction details for these assemblies are shown in figure 9.

A thoriated nickel disc is welded to the platinum-rhodium thermocouple and separates it from the coated surfaces. This disc provided contact with the coated sheet material and did not react with either the coating or the thermocouple at 2,400° F. Ceramic fiber insulation is used to reduce heat flow down the alumina protection tube. This spring-loaded alumina tube provides electrical insulation and transfers the contact force from the cold spring to the thermocouple contact disc.

#### CONCLUDING REMARKS

In conclusion, the successful application of coated refractory metals, particularly in thin gages, for structural components requires definition of the important coating-substrate environment interactions such as the effect of coating and subsequent high-temperature exposure on the mechanical properties of the composite. Although these preliminary investigations with small coated specimens are indicative of coating development and aid in coating selection, the evaluation of a representative structural component, when subjected to the



fabriation procedures and thermal stresses which are typical of the intended application, is necessary to define the performance selected coating-substrate composite as a structural material.

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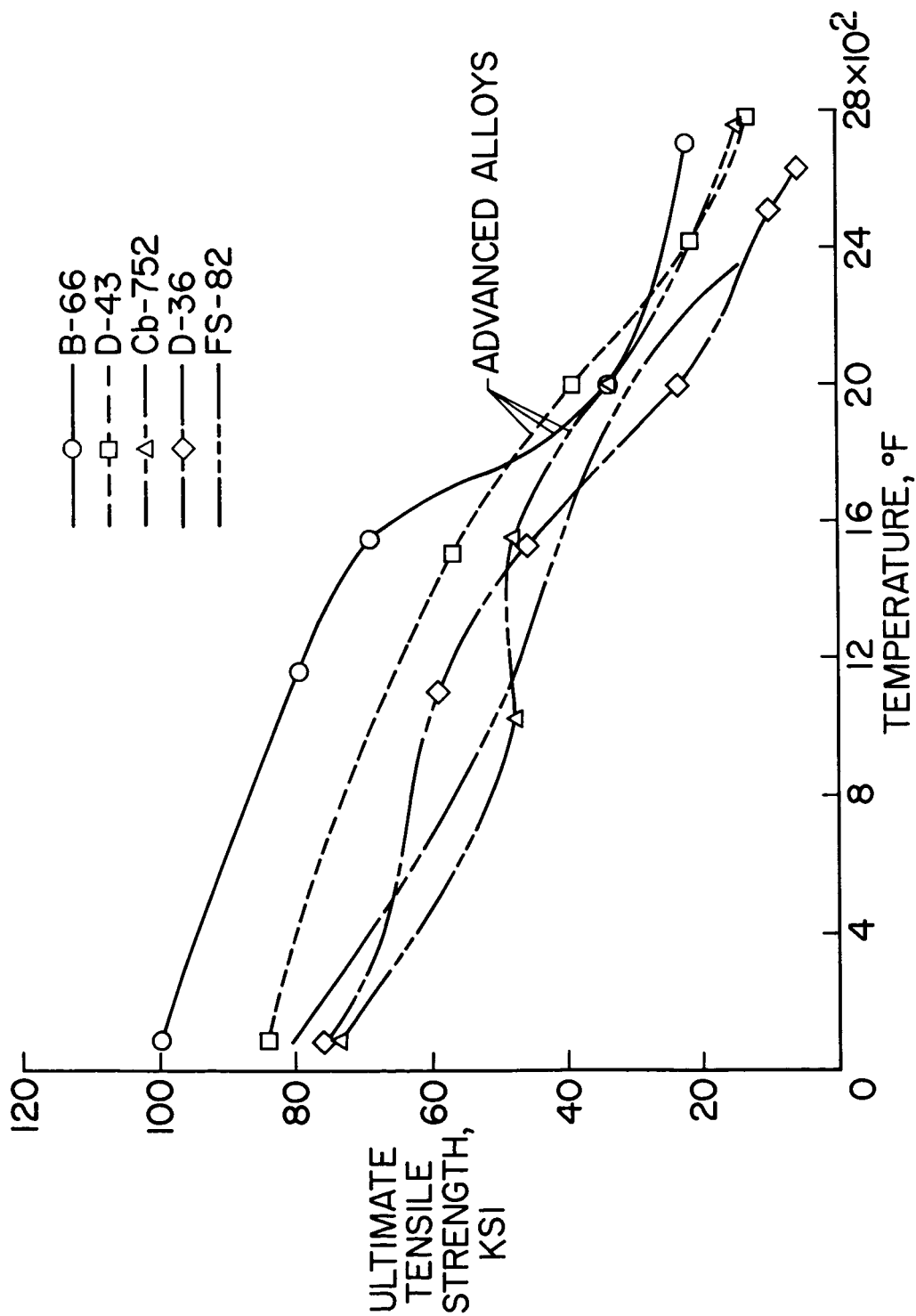


Figure 1.- Tensile strength of selected columbium alloys.

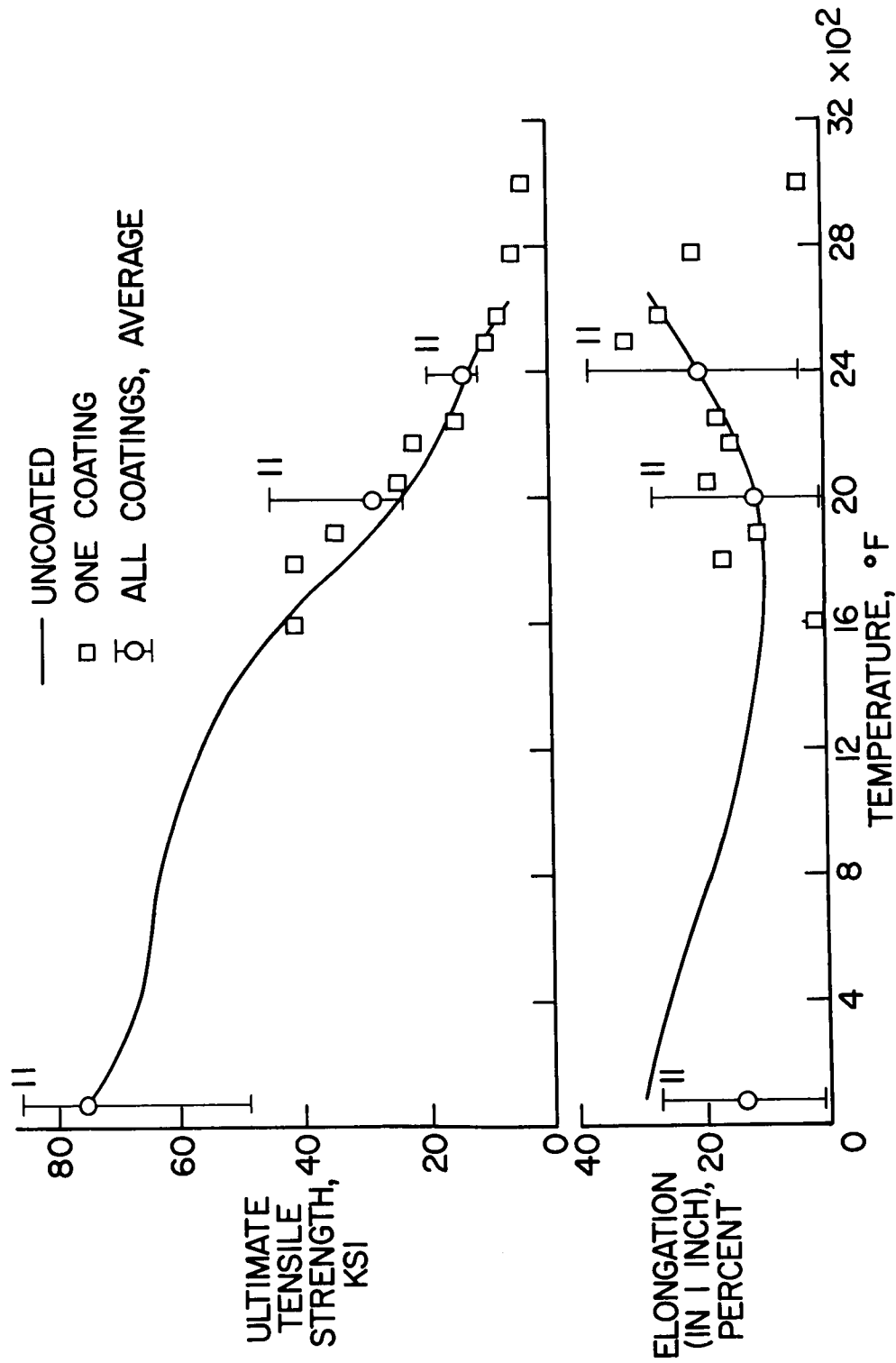
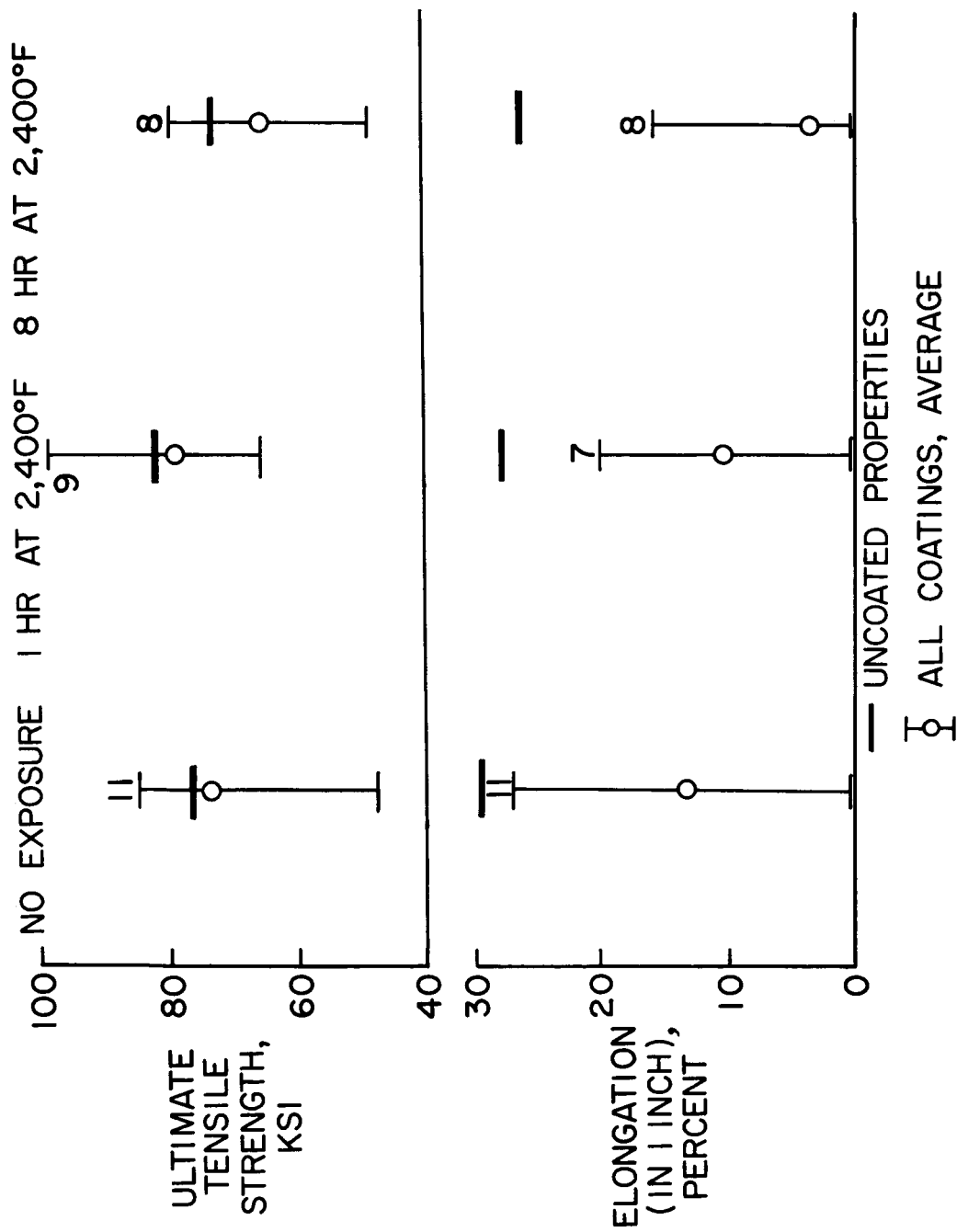
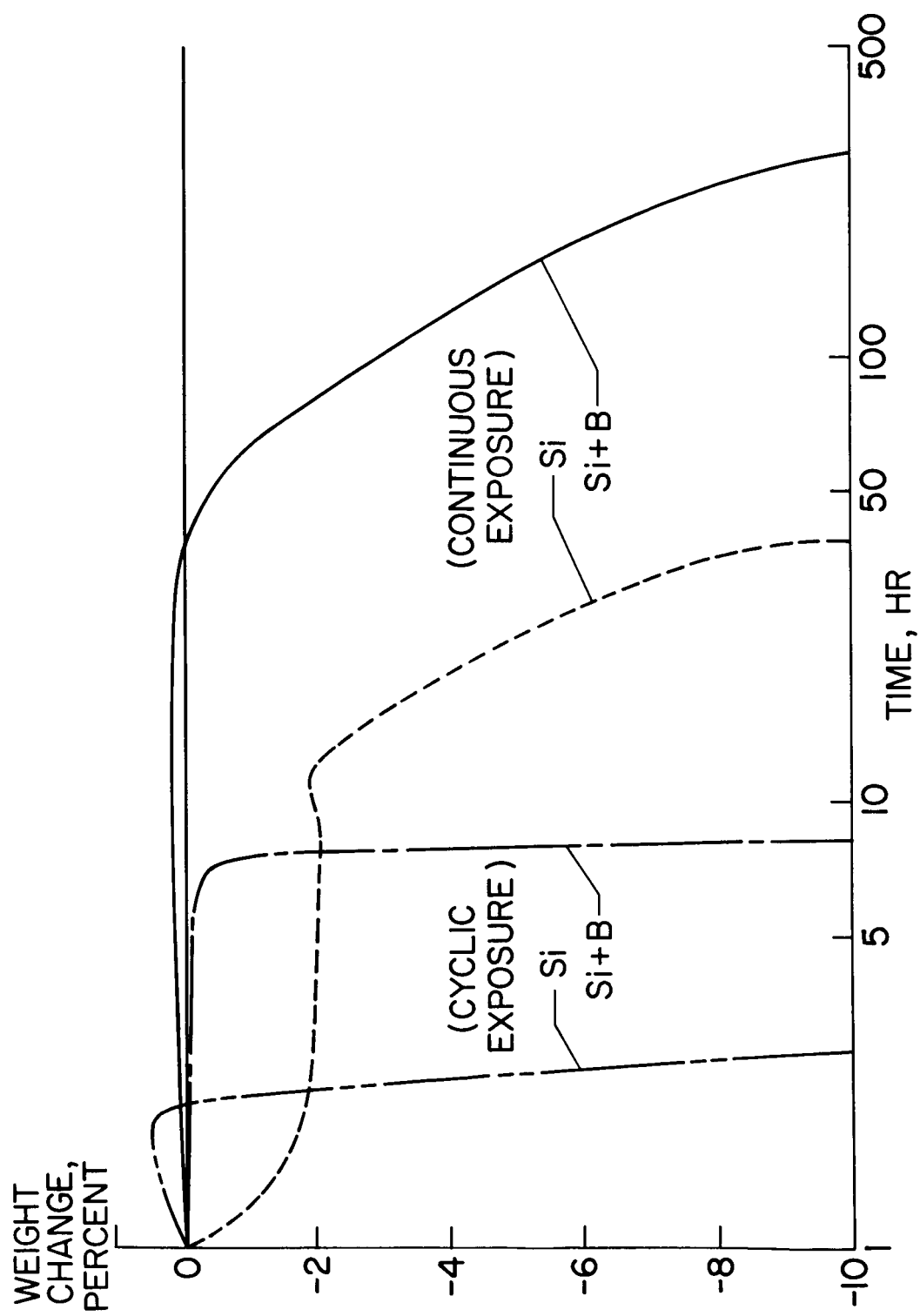


Figure 2.- Effect of coating application on tensile strength and elongation of D-36 columbium alloy.



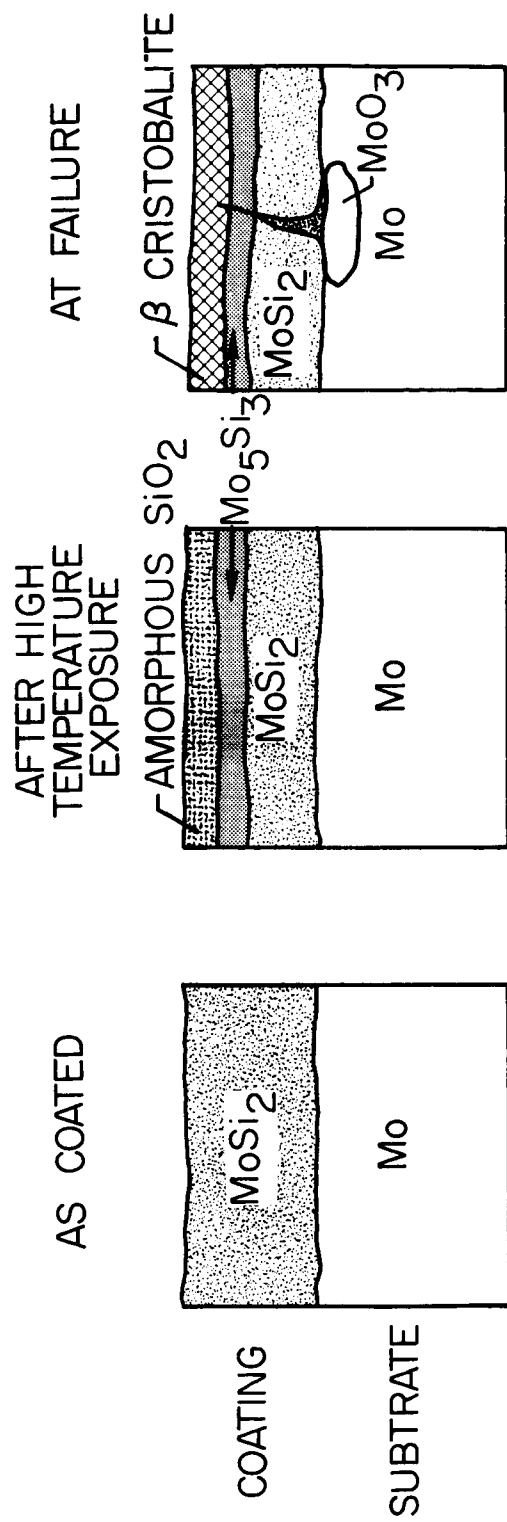
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Figure 3.- Effect of 2,400° F exposure on tensile strength and elongation at room temperature of bare and coated D-36 sheet.

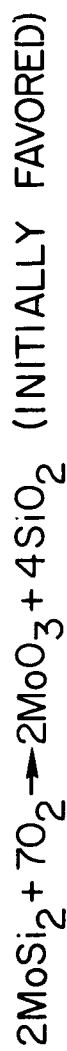


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Figure 4.- Typical specimen weight changes for two types of silicide based coatings on Mo-0.5Ti during both continuous and cyclic exposure to 2,500° F in air.



#### OXIDATION REACTIONS FOR MoSi<sub>2</sub>



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Figure 5.- Phases present in silicide coated molybdenum.

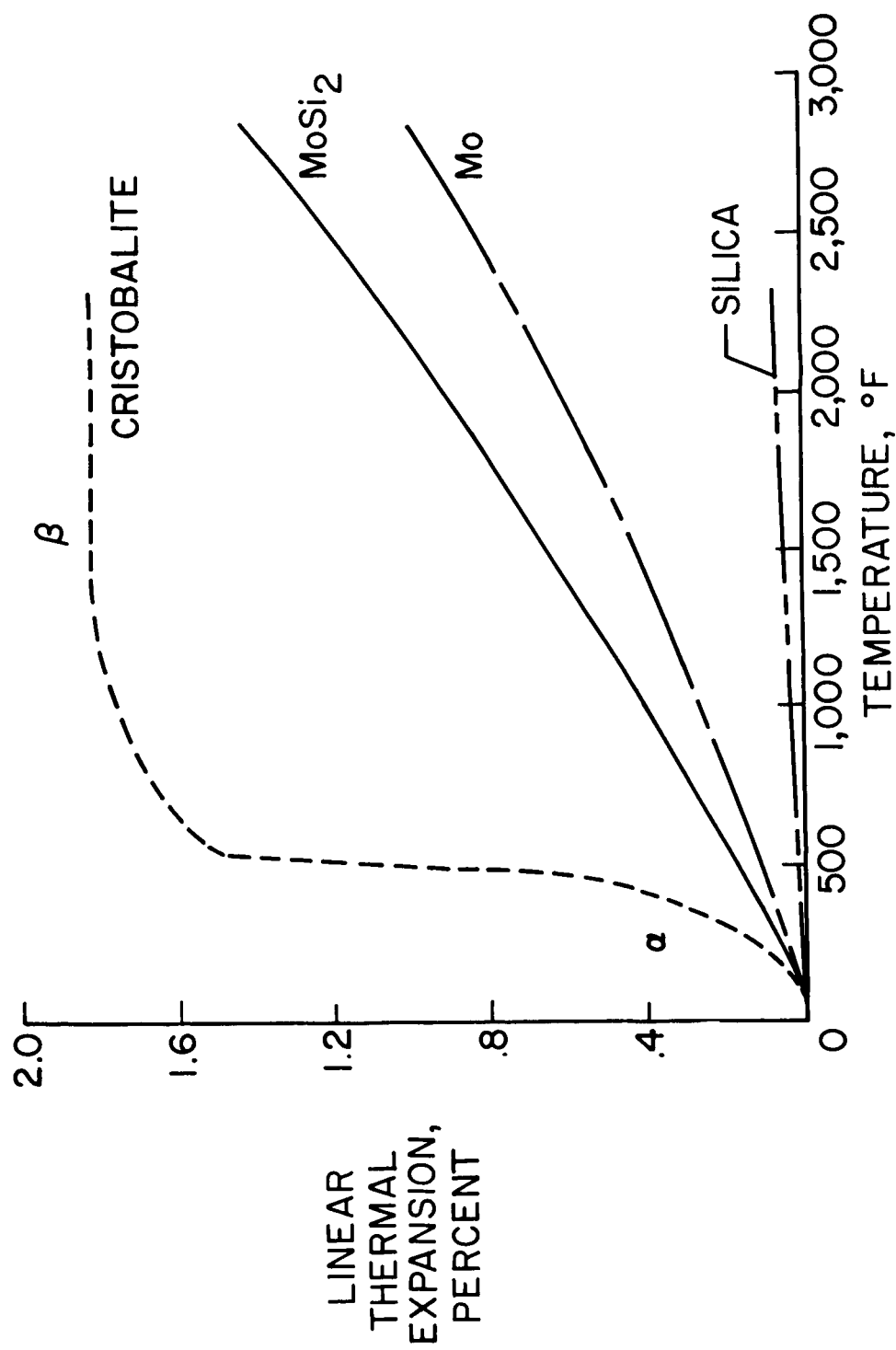
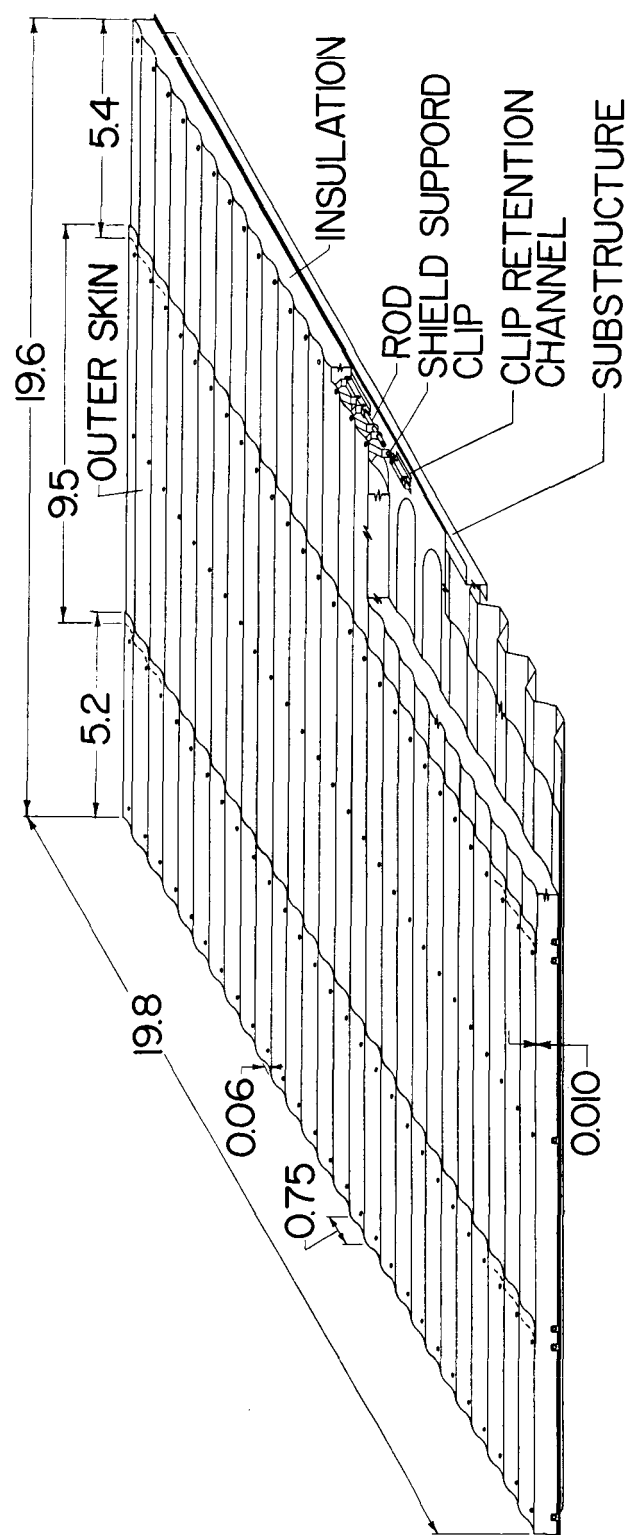


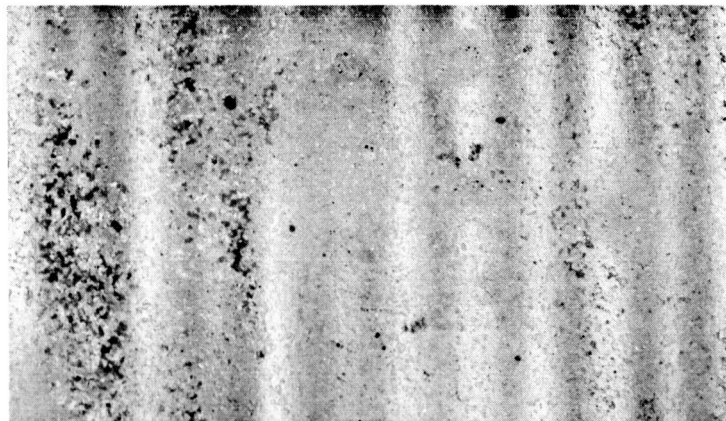
Figure 6.- Linear thermal expansion of selected materials.



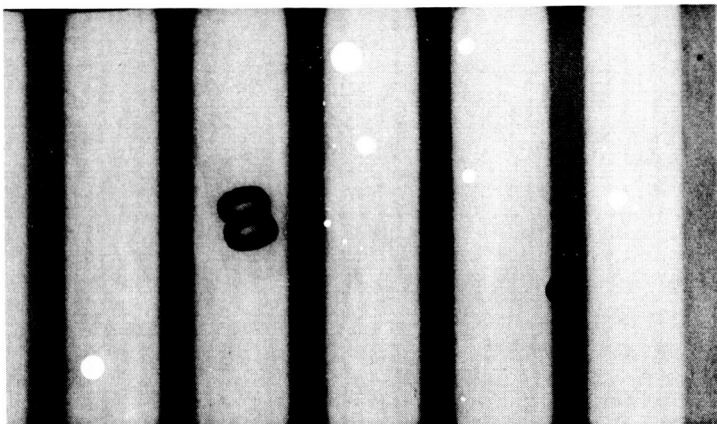


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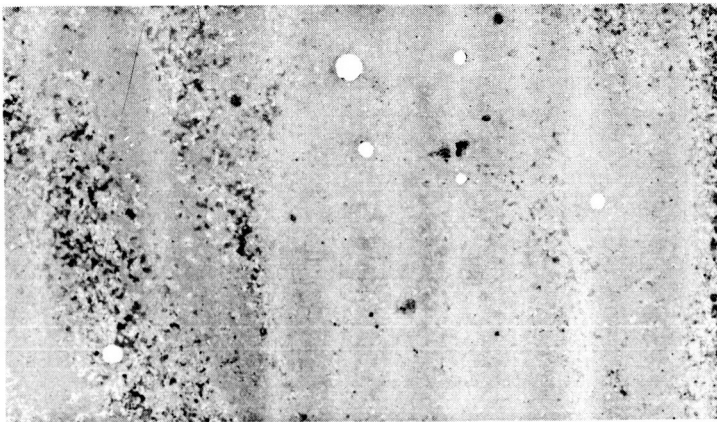
Figure 7.- Design details of heat shield panels. All dimensions are in inches.



(a) Photograph shows no visible damage.



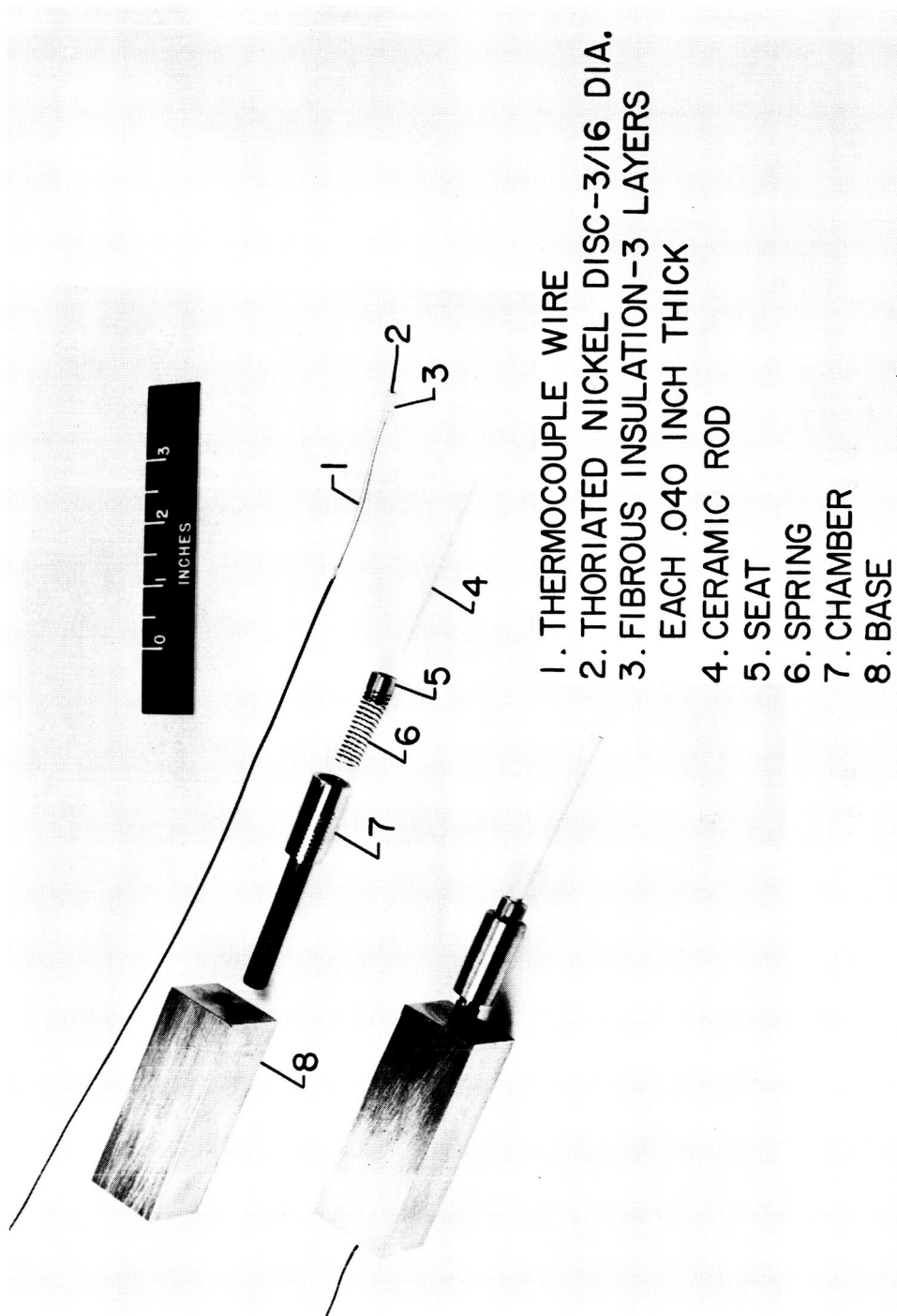
(b) Radiograph indicates oxidation damage.



(c) Photograph showing damaged areas with coating removed.

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Figure 8.- Radiographic detection of oxidation damage to a coated molybdenum-alloy heat shield.



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Figure 9.- Spring-loaded thermocouple probe.